

## **Relaxation Time of Molecules of Amino Acids Using the Modulated Technique**

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### **Abstract**

The relaxation time of molecules of amino acid for protonation reaction of lysine has been measured using a modulated temperature technique.

### **1. Introduction**

There have been several studies made on the kinetics of protonation reactions of various amino acids using either NMR methods (1) or modulated technique (2 and 3). A detailed study has therefore been undertaken of the rate constants of lysine protonation reactions.

### **2. Experimental**

Rate constants were derived from the experimental data as outlined previously (3, 4). All measurement were taken in a pH of a range between 4.5 to 6.6 pH of the samples were adjusted with NaOH or HCl as appropriate. The concentration range of the aqueous lysine solutions was 0.03125 to 0.25 M and all measurements were at 20°C. In all cases only one relaxation time was observed for each sample.

### **3. Result and Discussion**

It was found earlier that for the amino acids, plots of inverse relaxation times vs. concentration of zwitterions at a constant pH, by this ratio of slope to intercept, the negative logarithm was equal to  $pK_1$  value of amino acids (4).

It can be assumed that lysine can be described by the same model used previously in the description of the amino acid (1, 3, 4).

Values of the measured rates constants are shown in (Table 1). The values for the glycine zwitterions are those obtained by us previously (5) using similar conditions to those in obtaining the values for lysine.

Our values are mainly similar to those of Sheinblatt and Gutowsky (1) except that the values of  $k_3$ ,  $k_4$  and  $k_5$  are somewhat lower.

$k_1$  for the lysine zwitterions is smaller than that for the glycine zwitterions,  $k_2$  is somewhat smaller,  $k_3$  is a little smaller,  $k_4$  and  $k_5$  are quite a lot smaller, and  $k_6$  is a little smaller. The  $pK_2$  values for glycine is in fact larger than that for lysine than glycine giving a simple explanation of  $k_1$ .

As I have pointed out earlier (5),  $k_2$  values appear to be a pH dependent which is contrary to what the analysis (1) indicates and there may be contributions to this constant from other unrecognized reaction. The free energy for this reaction is very low indeed (5) making the reaction apparently quite different from all the other protonation reaction whilst these  $k_2$  values are of the right order for diffusion controllers reactions. Whilst these  $k_2$  values are of the right order for diffusion controlled reaction.

The activation energy for the  $k_5$  reaction in glycine is particularly his (5) and indeed this is the only one of the zwitterions protonation reaction in which the entropy of activation plays a minor role. In this case I assume that the activation energy of the reaction is smaller for lysine than for glycine. Sheinblatt and Gutowsky (1) have explained differences between  $k_5$  for lysine and glycine in terms of the relative acidities.

$k_3$  and  $k_4$  are both constants for bimolecular reaction leading to the identical outcome.

**Table 1:** The rate constants of lysine and glycine\*at 20°C

Rate Constant	Lysine	Glycine*
$k_1 \text{ Sec}^{-1}$	$4.35 \pm 0.9$	4.99
$k_2 \text{ M Sec}^{-1}$	$1.59 \times 10^{11} \pm 0.2$	$1.76 \times 10^{11}$
$k_3 \text{ M Sec}^{-1}$	$77.2 \pm 0.1$	79.5
$k_4 \text{ M Sec}^{-1}$	$1.18 \times 10^7 \pm 0.12$	$1.95 \times 10^7$
$k_5 \text{ M Sec}^{-1}$	$2.73 \times 10^7 \pm 0.09$	$7.44 \times 10^7$
$k_6 \text{ Sec}^{-1}$	$179 \pm 0.8$	183

\*Ref. (5).

#### 4. Conclusion

The behavior of lysine is not different in kind from that of amino acids. It seems to be well described by a Sheinblatt and Gutowsky (1) type analysis. Specific differences in magnitude of rate constants can be explained in the cases where the reactions are entropy dominated, by the acidities of participating groups.

In the case of protonation reactions dominated by the enthalpy of activation, this appears not to be so. Therefore the measurement of rate constants of protonation reaction alone is not always sufficient to explain these reactions.

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## **References**

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